



Investigation, modelling and reviewing the effective parameters in microwave-assisted transesterification



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ABSTRACT

Synthesis of biodiesel using so-called microwave (MW) energy at a frequency of 2.45 GHz is investigated in this work. In this frequency, energy can transfer in the scale of molecular size. Dipolar rotation and ionic conduction are two important mechanisms of energy transformation; Thus, an efficient and localized high temperature is produced that can assist reaction. In this study, we focused on effective parameters during transesterification. It was found that methanol produces a higher yield than the other alcohol types. It is due to methanol reorientation ability under the microwave irradiation, which may result in a better microwave absorption. Furthermore, the requirement for catalyst in this situation was reduced about ten-fold. Besides, an empirical model was generated to analyze and predict the effect of operating parameters. The model was based on fitting a wide range of different experimental results for homogeneous alkalic catalysis. The predictive power of developed model was within the temperature range of 40 and 80 °C, reaction time between 5 and 15 min and alcohol to oil molar ratio between 3 and 12. The optimum values in the mentioned ranges included the alcohol to oil molar ratio of between 1:6 to 1:9 in homogenous catalyst systems and 15:1–18:1 in heterogeneous one, reaction time within 3–5 min and the temperature within 65–90 °C. Finally a very good agreement between the model and experimental data was observed with error of $\pm 8\%$ even with the other catalysts types.

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1. Introduction

In recent decades, increasing consumption rate of fossil fuels has resulted in discharge of these resources. Thus, alternative fuels have attracted much attention and among them Fatty Acid Methyl Ester (biodiesel) is one of the best choices. Biodiesel is a clean burning fuel which is produced from renewable sources [1]. This fuel is biomass-based with excellent lubricating properties. It does not contain toxic compounds such as aromatic hydrocarbons, metals, sulfur or crude oil residues [2]. Therefore, it is a good replacement for petroleum based diesel by reducing Volatile Organic Compounds (VOC) emissions and Green House Gases (GHG) [3]. It can be blended with fossil diesel at any ratio and used for diesel engines without any modification [4]. Furthermore, biodiesel is safer than petroleum diesel since it is non-flammable and non-explosive, with the flash point of 150 °C in contrast to petroleum diesel with the flash point of 64 °C [5]. Several methods have been suggested to produce biodiesel such as: Thermal cracking (pyrolysis), Microemulsification, Direct use of vegetable oil and Transesterification. In thermal cracking, one substrate is converted into another using heat along with a typical catalyst or only heat in absence of oxygen or air. In microemulsification, the viscosity of vegetable oils decreases by mixing them with solvents, such as alcohols and ionic or non-ionic amphiphiles. Both these procedures may result in imperfect combustion because of their low cetane number. The biodiesel obtained from the direct usage of vegetable oil, suffers from high viscosity which can damage the actual diesel engine [6]. Transesterification (or alcoholysis) is the most common and simplest process, which is widely studied [6–8]. This method contains three steps for exchanging the alkoxy group of an alcohol with the alkoxy group of an ester compound. In the first step, triglyceride molecule existing in animal fats or vegetable oils reacts with an alcohol in the presence of a catalyst and leads to diglyceride and one molecule of ester. In the next step, diglyceride with another alcohol molecule converts to monoglyceride. Finally, monoglyceride with the third alcohol molecule produces glycerin. In each step, one fatty acid ester molecule is generated [6,9,10]. Today, the majority of biodiesel in industry is produced by transesterification. However, there are some obstacles related to this method:

- Most commercial processes are done in a batch system which lessen some advantages of continuous mode.
- Transesterification may take 1–24 h to reach a high fatty acid methyl ester yield or oil conversion.
- Generally, it is nearly 1.5 times more expensive than petroleum diesel fuel [11].
- There is an upper conversion limitation in the absence of product removal since transesterification is a reversible reaction [4,11].
- The immiscible nature of reactants is another limitation of mass transfer [12].
- The other problem within the biodiesel production is energy consumption.

There are several techniques to compensate for these weaknesses such as increasing alcohol to oil molar ratio and catalyst concentration as well as adding co-solvent in the reaction, such as tetrahydrofuran or working under supercritical conditions (temperatures above 300 °C and pressures above 40 MPa). All these mentioned factors are used to increase the mass transfer between the two immiscible phases (called oil and alcohol as reactants) [12]. However, the addition of co-solvents increases the number of process steps and energy consumption. In supercritical process, methanol needs high temperature and pressure for a long time, which may result in significant loss of unsaturated fatty acid ethyl ester (FAEE) due to degradation reaction. Based on the report of

Patil et al. [7], the alkyl esters and oil/lipid tend to become thermally unstable or decompose in transesterification with temperature above 255 °C at a fixed pressure of 1200 psi [7]. In the above mentioned methods (of transesterification), the required energy of the reaction is provided by convection, conduction and radiation of heat energy from the surfaces of the reactor to the reactants; it is an inefficient heat transfer [13]. Recently, several technologies have been introduced to attain a precise mixing and mass transfer in the reaction system to decrease the need of energy resources. These new technologies are based on the use of alternate energy sources in a special wavelength such as microwave or ultrasound energy. In essence, the microwave energy interacts with the molecules at a very fast rate, thus localized superheating is generated. Therefore, the real reaction temperature is higher than the average temperature of the medium [14]. In consequence, both of the reaction time and energy consumption are reduced by means of microwave irradiation [13]. Then microwave heating becomes more efficient over conventional methods (Table 1). Because by these methods energy is transferred into a sample depends upon convection currents and the thermal conductivity of the reaction mixture, which is relatively slow and inefficient [15]. In addition, it can overcome the major problems of conventional heating such as limitations depend on the thermal conductivity of materials, heterogenic heating of the surface, specific heat and density [11]. It also requires less energy input for heating compared with the conventional heating method [16].

However, there is no doubt that microwave heating suffers from some challenges. Microwave radiation cannot support a very large reaction vessel due to its penetration depth limitations. Therefore, scaling up the new technique is still an unsolved problem. For example, Groisman and Gedanken reported that the efficiency of laboratory batch ovens is higher than a continuous flow system at various microwave powers [17]. Uncontrolled heating is another problem, which may lead to safety concerns in industrial vessels. Unfortunately, there are few published works in this field, thus this field has not received sufficient attention [13]. In this paper, we have gathered the result of the majority of published papers in microwave systems and investigated the effect of key parameters such as temperature, microwave irradiation power, alcohol to oil molar ratio, catalyst and its concentration. Besides highest and most optimal results of all published works, containing different alcohols and catalysts (homogenous or heterogeneous) are summarized in several tables for a better judgment. For the other information from more than 1000 of experimental tests (with optimum or non-optimum results), an empirical correlated equation has been developed for a wide range of parameters. The model predicts satisfying agreement with the experimental data and can be useful for the other authors to be able to estimate their own experimental result before doing the test.

2. Microwave irradiation

Microwaves are non-ionizing radiations i.e., electromagnetic waves that can be transmitted, reflected or absorbed [15]. Thus,

Table 1
Comparison between convection and microwave heat transfer.

Microwave energy	Conventional energy
Energetic coupling	Conduction/convection
Coupling at the molecular level	Superficial heating
Volumetric	Superficial
Rapid	Slow
Dependent of the properties of the material	Less dependent
Selective	Nonselective

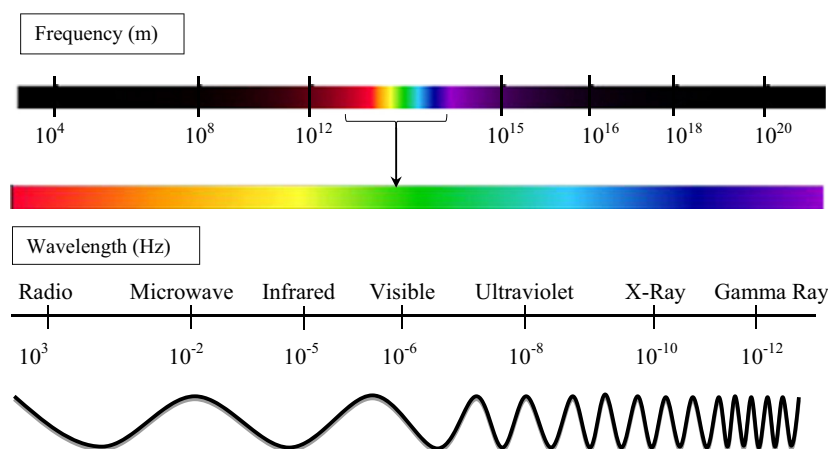


Fig. 1. Frequency and wavelength of microwave radiation region.

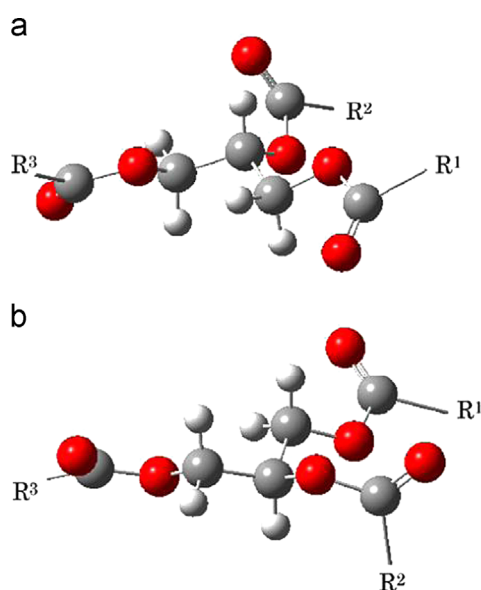


Fig. 2. Conformational isomers of triglyceride [10]. (a) Molecule with a lower dipole moment. (b) Molecule with a higher dipole moment.

these are unconventional energies which are transferred directly to the reagents [16].

Microwaves (MW) have the wavelengths between 1 mm and 1 m depending on the frequencies between 0.3 and 300 GHz. In electromagnetic radiation spectrum, the microwave radiation region is located between infrared radiation and radio waves (Fig. 1) [15]. In order to prevent any interference with cellular phone frequencies and telecommunications, the frequency of 2.45 GHz, which corresponds to a wavelength of 12.25 cm, is used for all domestic microwave ovens and chemical syntheses. The microwave heating is caused by the interaction of the electric field of radiation with the matter that can affect molecular actions, such as dipole rotations or ions migration. But, they cannot ionize the atoms crossed or change the molecular structure due to their low energy content [14]. Actually, it has a selective heating function. In other words, non-polar molecules are inert in the microwave electric fields while polar molecules with high dielectric constant and low molecular weight can selectively absorb microwave energy [11]. This selective heating of certain compounds may lead to the formation of microzones with a temperature much higher than the overall recorded temperature of the reaction bulk mixture. These high temperature microzones are called “hot spots” [13]. Thus a rapid enhancement of temperature is produced which

may lead to an increase in the acceleration of chemical reaction rate [14]. For chemical reactions such as transesterification, that use microwaves as a means of heating, the polar molecules may bring more advantages [18].

Generally, two mechanisms of dipolar rotation and ionic conduction have been introduced for the interaction between microwave energy and the mixture. The first mechanism will take place if the molecule has a dipole moment. In this case the dipole tries to align with the applied electric field which results in a continuous arrangement of the dipoles by its persistent fluctuation [15]. This continual reorientation of the molecules results in an increase in friction, kinetic energy and finally the production of heat in the sample. At 2.45 GHz, molecules can align with the electric field in sufficient time; however, it cannot follow the oscillating field exactly [15]. The second mechanism is occurred when a charged molecule is exposed to the electric field. In this case the microwave irradiation moves the ions back and forth through the sample and results in clashing them into each other and generating heat. These mechanisms contribute to localized superheating result in high temperature gradients. At the same time, the probability of molecular encounters increases by accelerating the molecular/ionic movement which leads to increased reaction rates [19]. The above mentioned methods both occur simultaneously in transesterification. Polar materials such as alcohol and triglycerides, etc., can absorb the microwave irradiation and the catalyst molecules such as NaOH can be divided into positive and negative ions.

3. Transesterification under the microwave irradiation

The schematic diagram of transesterification using methanol has been shown in Eq. (1) with the support of Figs. 2 and 3. R^1 , R^2 and R^3 , in this equation represents alkenyl and alkyl groups. They can change into the number of carbon atoms and their double bonds. As it is clear there are several C–O and C–C single bonds near the three-ester bonds in the triglyceride molecule. By rotation of these bonds, different types of conformational isomers with different momentary dipole can be produced. In this situation, different directions of three oxygen atoms of C=O bonds can be produced. Under the microwave irradiation, rotation around C–O or C–C bonds occurs in the case of polar molecules. Thus the polarization of C=O bonds, which have higher electronegativity within the molecule and are active under microwave irradiation, occurs in the molecule. Then C=O bonds try to be scattered in an electromagnetic field as shown in Fig. 2. Therefore, the dipole moment of a triglyceride molecule becomes smaller under microwave spectrum

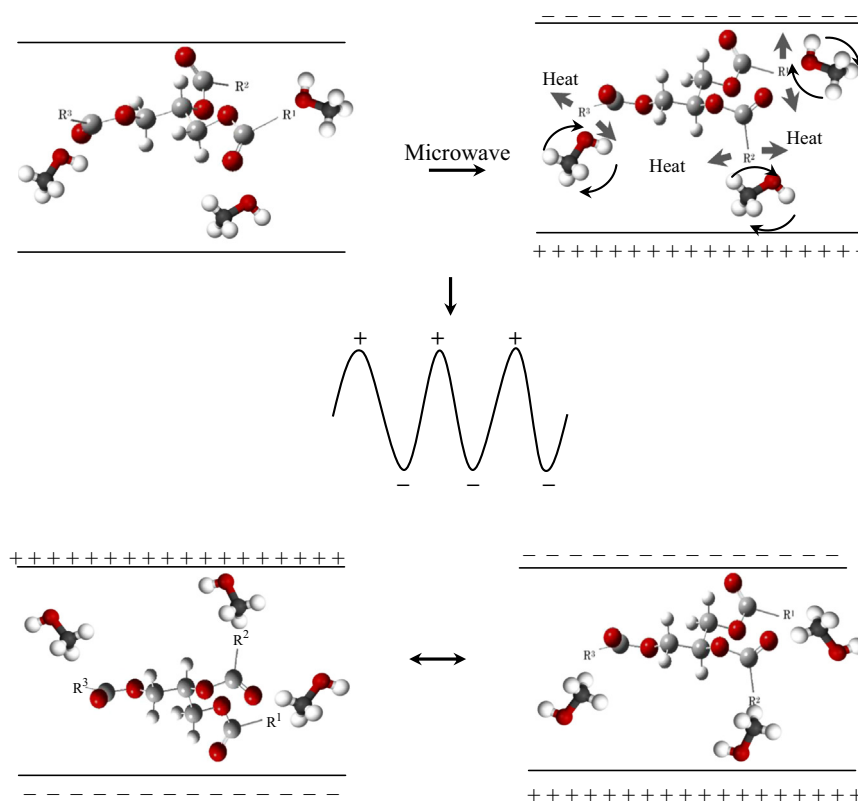
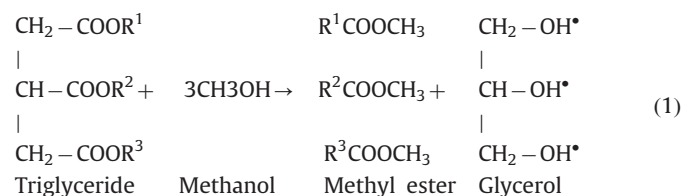


Fig. 3. Effect of Microwave irradiation on molecular situation. \bullet : H, \bullet : C, \bullet : O.

irradiation. Theoretically Asakuma et al. [10] found out that to enhance the momentary dipole to the higher level, 26.9 kcal/mol energy is demanded; and after stopping the irradiation, the lower molecular structure with the lower dipole moment is retained momentarily [10]. Polar groups under this situation (microwave field with the frequency of 2.45 GHz) rotate frequently. It is worth mentioning that, since the electronegativity of the oxygen is much higher than that of an alkyl group, the R groups do not have any relative effect on the different dipole moment of the molecule [10].



3.1. Effects of different alcohol types

The interaction between the reaction compounds and microwave irradiation, which results in increase of dipolar polarization phenomenon, can significantly reduce the activation energy. Essentially the amount of the reduction depends on the reaction mechanism and the component ability to absorb the microwave. The amount of the absorption of microwave energy by molecules depends on their reorientation ability under the microwave radiation. Referring to Tables 2–5, it is clear that methanol is preferred by most of the researchers during transesterification process. Yuan et al. [20], used both methanol and ethanol under microwave radiation for less than 120 min at the temperature of 338 and 351 K, respectively. They reported that the reaction yield of methanolic system was higher than the ethanolic one at the

same time. In addition, the ethanolic system reached an equilibrium situation after 120 min and the methanolic system after 60 min. Another point mentioned by Kanitkar [19] is the easier formation of methyl ester in comparison with ethyl ester. It is because of the different reactivity of alcohols with catalysts in order to produce alkoxide ion for both soybean and rice bran oil.

Therefore, they significantly obtained higher methyl ester conversion compared to ethyl ester which leads in less requirement for methanol to oil molar ratio in contrast with ethanol [19]. Kanitkar also observed that for both rice bran and soybean oil, there is a less activation energy need for methyl ester than for ethyl ester formation. Terigar et al. [21] also reported the same issue. Such results indicated that methanol has a stronger ability to absorb the microwave spectrum compared to ethanol [7,20]. Dielectric properties were both frequency and temperature dependent. However, oils as the non-polar materials are unaffected by the variations in frequency and temperature. Dielectric constant was lower for ethanol than that for methanol throughout the frequency range. Dielectric loss for ethanol at higher frequencies (> 1000 MHz) was lower than methanol and higher at lower frequencies (< 1000 MHz). Muley et al. [22] have also found that the dielectric properties were lower for ethanol catalyst mixture than that for methanol–catalyst mixture throughout the frequency range. They have also observed that the decreasing rate of dielectric constant with frequency was greater for ethanol compared to methanol. At 60 °C the decrease of the dielectric constant of ethanol is from 28 to 23 for the constant frequency range. They have justified that, the dielectric constant decreases by increasing the number of CH₂ groups in R–OH chain. A combination of hydrogen and carbon in the hydrocarbon portion of a molecule is non-polar. But, when an oxygen atom bonds with a hydrogen atom, the electron distribution in the newly formed molecule changes and induces a dipole moment that alters the polarization. Therefore, methanol is more polar because of its smaller molecular

Table 2
Homogenous alkaline catalysts used for transesterification reaction assisted by microwave irradiation.

Power (W)	Feedstock	Alcohol (oil molar ratio)	Temp. (°C)	Catalyst (wt%)	Time (min)	Conversion (%)	Remarks	Ref
Step 1, 300 Step 2, 125 200	Seed oil	Methanol(6:1)	60	KOH (0.5%)	5	89.5	1 min to reach 50 °C at 300 W 30 s to reach 60 °C at 125 W	[51]
70	Soybean oil	Methanol(12:1)	70	KOH (1%)	2	96.26	Optimum	[13]
70	Soybean oil	Methanol(12:1)	70	KOH (1%)	7	99.53	Maximum	
CON	Soybean oil	Methanol(9:1)	73	KOH (1%)	3	96.5	Maximum	[13]
CON	Soybean oil	Methanol(9:1)	66	KOH (1%)	2.5	43.1	Thermostatic bath	[13]
CON	Soybean oil	Methanol(9:1)	67	KOH (1%)	3	78.8	Continuous process	
CON	Soybean oil	Methanol(9:1)	68	KOH (1%)	4	88.2		
CON	Soybean oil	Methanol(9:1)	72	KOH (1%)	7.5	93		
CON	Soybean oil	Methanol(9:1)	75	KOH (1%)	14.5	91.6		
CON	Soybean oil	Methanol(9:1)	68	KOH (1%)	15	88.7	Heating plate discontinuous process	[13]
CON	Soybean oil	Methanol(9:1)	72	KOH (1%)	30	91.3		
CON	Soybean oil	Methanol(9:1)	75	KOH (1%)	60	96.6		
Step 1—300 Step 2—125	Pinnata seed oil	Methanol(6:1)	60	KOH (0.5%)	5	89.5	1 min to reach 50 °C at 300 W and 30 s to reach 60 °C at 125 W	[51]
		Methanol(6:1)	60	KOH (1%)	5	97.0 ^a		
		Methanol(6:1)	60	KOH (1%)	3	88.6		
		Methanol(6:1)	60	KOH (1%)	5	96.0		
		Methanol(6:1)	60	KOH (1%)	7	96.0		
		Methanol(6:1)	60	KOH (1%)	10	97.5		
		Methanol(6:1)	60	KOH (1.5%)	5	96.0		
CON 1200	Seed oil	Methanol(6:1)	60	KOH (1%)	3 h & 5 min	97	–	[51]
	Jatropha oil	Methanol(7.5:1)	65	KOH (1%)	30	83	Optimum	[52]
	Jatropha oil	Methanol(7.5:1)	65	KOH (1%)	30	94.5	Maximum	
	Jatropha oil	Methanol(7.5:1)	65	KOH (1.5%)	60	99.95	Maximum	
500	Yellow horn	Methanol(6:1)	60	KOH (1%)	6	96	Maximum	[9]
120	Nagchampa oil	Methanol(6:1)	88	KOH (1%)	15	~90	Optimum	[53]
Sonication	Nagchampa oil	Methanol(6:1)	50	KOH (1%)	20	~90	Optimum	[53]
CON	Nagchampa oil	Methanol(6:1)	90	KOH (1%)	90	~90	Optimum	[53]
1300	Seed oils	Methanol(6:1)	50	KOH (1%)	7.2	98	7.2 L/min (continuous)	[54]
1200	Cooking oil	Methanol(6:1)	65	KOH (1%)	2	100	Optimum	[15]
CON	Cooking oil	Methanol(6:1)	65	KOH (1%)	60	96	Optimum	[15]
252	Cottonseed oil	Methanol(6:1)	60	KOH (1.5%)	7	89.5–92.7	Optimum	[31]
252	Cottonseed oil	Methanol(6:1)	60	KOH (1.5%)	30	78.9–99.8	Optimum	[31]
252	Cottonseed oil	Methanol(6:1)	50	KOH (1.5%)	6	99.7	Maximum	[31]
		Methanol(6:1)	55	KOH (1.5%)	7	99.8	Maximum	
		Methanol(6:1)	60	KOH (1.5%)	6	99.8	Maximum	
			65	KOH (1.5%)	5	99.8	Maximum	
CON	Cottonseed oil	Methanol(6:1)	60	KOH (1.5%)	30	99.9	Maximum	[31]
		Methanol(6:1)	60	KOH (1.5%)	60	99.9	Maximum	
		Methanol(6:1)	60	KOH (1.5%)	75	99.9	Maximum	
400	Dry algal biomas	Methanol(12:1)	62	KOH (2%)	4	63.19	Optimum	[23]
300	Crude palm oil	Methanol(6:1)	78	KOH (2 %)	5	95	Optimum	[55]
CON					60	95		
100	Karanja oil	Methanol (40 wt%)	62	KOH(3%)	6	69	Optimum	[56]
180	(<i>Pongamia</i>					75	Optimum	
300	<i>pinnata</i>)					80.48	Optimum	
600	Triolein	Methanol(6:1)	50	KOH (5 %)	1	98	Optimum	[44]
375	Used frying oil	Ethanol(6:1)	60	KOH(1%)	4	100	Optimum reduced the reaction time from 75 min to 4 min	[57]

600 W	Vegetable oil	Methanol(6:1)	50	KOH (1%)	–	97.9	Optimum, continuous 2 L/min	[54]
1200 W	Cottonseed oil	Methanol (6:1)	60	KOH(1.5%)	30	91.4	Optimum	[31]
70 W	Palm oil	Ethanol(6:1)	60	H ₂ SO ₄ (1 wt%) KOH (1.5wt%)	60	–	Esterification step 1. Two steps	[58]
		Ethanol(8.5:1)			5	85	Optimum	
70 W	Palm oil	Ethanol(24:1)	60	H ₂ SO ₄ (4 wt%) KOH (1.5 wt%)	60	–	With an ester content of 98.1 wt%	[58]
		Ethanol(4:1)			5	97.4	Optimum	
804 W	Rapeseed	Methanol(6:1)	40	KOH (1 wt%)	1	93.7	Maximum	[45]
600 W	Triolein	Methanol(6:1)	50	KOH (5 wt%)	1	98	Maximum	[44]
80	<i>Jatropha curcas</i>	Methanol(10.74)	62	NaOH (1.26%)	–	99.63	Optimum/	[30]
Step 1–300	<i>Pongamia</i>	Methanol(6:1)	60	NaOH (0.5%)	5	96	Continues 1.62 ml/min	
Step 2–125	<i>pinnata</i> seed oil			NaOH (1%)	3	91.2	Optimum	[51]
				NaOH (1%)	5	93	Maximum	
				NaOH (1%)	7	96	Maximum	
				NaOH (1%)	10	95.3	Maximum	
1.6 kW	Soy bean	Methanol(5:1)	80	NaOH (15–18 wt%)	20	98.64	1 min to reach 50 °C at 300 W and 30 s to reach 60 °C at 125 W	
2.45 GHz	<i>Jatropha</i> oil	Methanol(12:1)	65	NaOH (1%)	7	89.7	Maximum	[19]
							Optimum	[32]
1250	WFPO	Methanol(12:1)	65	NaOH (1.5%)	7	97.89	Reduced the reaction time from 30 min to 7 min	
							Optimum	[32]
804	Rapeseed	Methanol(6:1)	40	NaOH (1%)	3	92.7	Reduced the reaction time from 30 min to 7 min	
300	Soybean oil	Methanol, 0.83 ml	60	NaOH (0.04 g)	1	95	Maximum	[45]
	3 g						Maximum	[59]
	Soybean oil	Methanol, 0.83 ml		NaOH (0.04 g)	5	94	Maximum	
	3 g							
	Rapeseed oil	Methanol,1.27 ml		NaOH (0.03 g)	1	95	Maximum	
	2.3 g							
1250	<i>Jatropha curcas</i>	Methanol (30:1)	55	NaOH (4%)	7	86.3	Optimum	[60]
1000	Rape seed oil	Methanol (9:1)	103	NaOH (0.1%)	6.5	98.5	Maximum	[37]
CON	Rape seed oil	Methanol (9:1)	65	NaOH (0.3%)	90	93.8	Maximum	[37]
600	Triolein	Methanol (6:1)	50	NaOH (5%)	1	98	Maximum	[44]
650	<i>Jatropha</i> oil	Methanol (30:1)	60	NaOH (4%)	7	86.3	Optimum	[60]
CON	<i>Jatropha</i> oil	Methanol (30:1)	60	NaOH (4%)	60–75	86.3	Optimum	[60]
1200	Corn soybean	Methanol (2.5:1 wt%)	140–150	2–20 mol% Diphenylammonium salt	10–20	100% obtained by h 5 mol DPAT	Maximum	[25]
1.6 kW	Soy bean	Ethanol (9:1)	80	NaOH (15–18 wt%)	20	98.32	Maximum	[19]
1.6 kW	Rice bran	Ethanol (9:1)	80	NaOH (15–18 wt%)	20	97.78	Maximum	
800	Used palm oil	Ethanol(12:1)	84.1	NaOH (3%)	1	90.6	Maximum	[61]
800	Used palm oil	Ethanol (12:1)	50	NaOH (3%)	30 s	97	Maximum	[61]
800	Used palm oil	Ethanol (12:1)	78	NaOH (3%)	30 s	97	Maximum	[61]
		Ethanol (9:1)		NaOH (1%)	30 s	83		
750	Frying oil	Ethanol (6:1)	60	NaOH (0.5%)	10 min	100	Maximum	[62]
800	Coconut oil	Ethanol (9:1)	78.5	NaOH (1%)	30 s	100	Maximum	[63]
	Rice bran oil			NaOH (1%)		94	Maximum	
	Used palm oil			NaOH (1%)		83	Maximum	
	Used palm oil			NaOH (1%)		92	Maximum	
	Kerosene (1:1 V/V)							
1100	Vegetable oil	Ethanol (9:1)	78	NaOH (1%)	10 s	100	Optimum	[64]
300	Safflower oil	Methanol (10:1)	60	NaOH (1%)	6	98.4	Optimum	[65]
750	Waste cooking oil	Methanol (6:1)	65	CH ₃ ONa (0.75 wt%)	3	96.6	30 min–86.3	[11]
							90 min–96.6	
800	<i>Jatropha</i>	Methanol (6:1)	70–73	NaOCH ₃ (1.0%)	30 s	96.5	Optimum	[66]
800	Used sunflower oil	Methanol (6:1)	60	NaOCH ₃	5	98.87	Maximum	[67]
800	continuous	Methanol(9:1)	70	[MorMeA][Br]	6	98	Optimum	[28]

Table 2 (continued)

Power (W)	Feedstock	Alcohol (oil molar ratio)	Temp. (°C)	Catalyst (wt%)	Time (min)	Conversion (%)	Remarks	Ref
800	Waste cooking oil	Methanol (6:1)	60	NaOCH ₃ (1.0%)	5	98.87%	Maximum	[68]
1200	Waste cooking oil	Methanol (15:1)	190	KOH (3 wt%)	10	26.1	Maximum	[69]
480	Dry algal biomass	Methanol (6:1)	88	KOH (1wt %)	15 min	60.9	Optimum	[70]
1100	High acid value Nagchampa oil <i>Jatropha curcas</i>	Ethanol	-	KOH (5 N)	13.28	89.31	Optimum	[71]

^a Optimum, the other values are the maximum one.

size and the shorter distance between the poles which allows it to rotate and realign faster. Furthermore the smaller molecules also have a higher dipole moment [22].

In the molecular structure of methanol, the OH group attached to a large molecule with the shortest chain length. Then methanol molecule is nearly spherical, which behaves as though it is anchored to an immobile raft. Thus at a particular frequency, it interacts better with the microwaves because it has a less molecular inertia and a lower gyration radius. In this situation it can spin faster and lead to higher reaction rates in comparison with ethanol [19]. Since the molecular structure of ethanol is completely non-symmetric, methanol is more rotational than ethanol at the microwave radiation [23]. Hence, methanol molecules have the dielectric loss-angle tangent of 0.659 at 2.45 GHz, and reorientate more rapidly than ethanol with the dielectric loss angle tangent of 0.25 under the microwave radiation [20]. In this situation the two-tier interface structure of methanol and oil is destroyed easier and the solubility of methanol in oil and localized superheating increases as well, which is another positive point for the conversion increase [23].

Another problem, which may arise during esterification, is the formation of stable emulsion during the radiation of microwave spectrum. For methanolysis, the formed emulsions may break down quickly to form an upper methyl ester and lower glycerol rich layers. But in ethanolysis, because of the presence of larger non-polar group in ethanol the formed emulsions are more stable. Then the production of biodiesel by using ethanol in alkali-catalyzed transesterification is more difficult [24]. As it is also indicated in Tables 1–5, methanol is more favorable for transesterification.

3.2. Effects of catalyst type and amounts of catalyst

A critical step in the synthesis of biodiesel under microwave irradiation is the selection of an appropriate catalyst. A correct choice along with desired conditions can assist the system to reach the best synthesis of process. Generally, vegetable or animal oil can be converted into methyl esters using either homogenous or heterogeneous catalysts. Heterogeneous ones are more applicable to produce cleaner processes; while, homogenous-based processes suffer from the presence of the other by-products, which decrease selectivity and increase the separation or purification time. Generally, transesterification is efficiently activated at much shorter time by assistance of MW irradiation in both of these situations in contrast with the conventional heating. As a serious decrement in the quantity of the by-products and separation time is obtained, energy consumption is reduced. In addition, the requirement for catalyst in transesterification process assisted by microwave technology is eliminated about ten-fold compared to the other transesterification methods [7,19,23].

3.2.1. Effects of homogenous catalysts

From Tables 2 and 3, homogenous catalysts are more popular in transesterification assisted microwave irradiation. This is due to the nature of MW irradiation, which is applicable in the molecular scale and is not able to suspend the heterogeneous particles in the system. Therefore another mixing type at the first step in such systems is required to help the catalyst particles to separate within the system. Among the homogenous type, both acidic and alkaline catalysts can convert the vegetable or animal oil into methyl esters. Under MW irradiation, both groups can be divided into their basic ions such as Na⁺, K⁺ and OH⁻ ions in alkaline as well as H⁺ and SO₄²⁻ ions in acidic groups. Therefore, they can be activated easily by microwave energy [9]. However, it is obvious from Tables 2 and 3 that alkaline catalysts are more popular due to

Table 3

Homogenous acidic catalysts used for transesterification reaction assisted by microwave irradiation.

Power/W	Feedstock	Alcohol/oil molar ratio	Temp. (°C)	Catalyst/loading (wt%)	Time (min)	Yield (%)	Remarks	Ref.
500	Yellow horn oil	Methanol(15:1)	60	H ₄ SiW ₁₂ O ₄₀ (1%)	10	96.2	Maximum	[27]
	Yellow horn oil	Methanol(15:1)	60	H ₄ SiW ₁₂ O ₄₀ (1%)	10	95.3	Maximum	
	Yellow horn oil	Methanol(15:1)	60	H ₃ PMo ₁₂ O ₄₀ (1%)	10	94.6	Maximum	
	Yellow horn oil	Methanol(15:1)	60	H ₄ SiMo ₁₂ O ₄₀ (1%)	10	92.8	Maximum	
200	Castor oil	Methanol(12:1)	65	H ₂ SO ₄ (5%)	10	43	Maximum	[20]
	Castor oil	Methanol(12:1)	65	H ₂ SO ₄ (5%)	20	54	Maximum	
	Castor oil	Methanol(12:1)	65	H ₂ SO ₄ (5%)	30	78	Maximum	
	Castor oil	Methanol(12:1)	65	H ₂ SO ₄ (5%)	90	88	Maximum	
	Castor oil	Methanol(12:1)	65	H ₂ SO ₄ (5%)	180	93	Maximum	
1200	Corn	Methanol(2.5:1)	150	DPAM (20%)	20	100	Maximum	[25]
	Corn	Methanol(2.5:1)	150	DPAM (10%)	20	99	Maximum	
	Soybean	Methanol(2.5:1)	150	DPAM (10%)	20	92	Maximum	
	Soybean	Methanol(2.5:1)	150	DPAM (8%)	20	86	Maximum	
	Corn	Methanol(2.5:1)	150	DPAM (5%)	15	78	Maximum	
	Corn	Methanol(2.5:1)	150	DPAM (5%)	20	53	Maximum	
1200	Corn	Methanol(2.5:1)	150	DPAB (10%)	20	96	Maximum	[25]
	Soybean	Methanol(2.5:1)	150	DPAB (9%)	20	97	Maximum	
	Corn	Methanol(2.5:1)	150	DPAB (5%)	20	84	Maximum	
1200	Corn	Methanol(2.5:1)	150	DPAT (10%)	20	100	Maximum	[25]
	Corn	Methanol(2.5:1)	150	DPAT (5%)	20	100	Maximum	
	Corn	Methanol(2.5:1)	150	DPAT (2%)	20	43	Maximum	
	Soybean	Methanol(2.5:1)	150	DPAC (10%)	20	7	Maximum	
	Soybean	Methanol(2.5:1)	150	DPAC (8%)	20	5	Maximum	

Diphenylammonium (DPA) catalysts contains, Tosylate(DPAT), Benzensulfonate(DPABS), Mesylate(DPAM), Chloride(DPAC) [25].

the corrosive nature of the acidic ones. Besides, they need a higher reaction time even under MW irradiation. But hydroxide catalysts usually decrease the yield of reaction because a small amount of water is often produced by mixing methanol with sodium- and potassium-hydroxides [15]. Then, water and free fatty acids can form soap (hydrolysis reaction), waste catalyst and decline catalyst effectiveness which is a problem [11]. This process also needs an extra step for purification. Just for information, some researchers in this step have used the microwave and reached satisfying results in a short time. This problem can be modified by acidic catalyst and since free fatty acids are additionally turned into methyl esters, it results in a higher conversion [25].

Refer to Table 3, among the acidic-based catalysts; sulfuric acid is a conventional acid catalyst in the transesterification. In comparison with the conventional systems, HPA catalyst is more effective under the microwave irradiation; because it can largely change to two hydrogen ions (H⁺) and sulfate ions (SO₄²⁻). Both can easily be activated under the microwave energy. In addition, all the other combinations of this acid (such as H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀, H₃PMo₁₂O₄₀, H₄SiMo₁₂O₄₀) are as powerful as the foundation under microwave spectrum irradiation. But their activity based on the order of acid strength decreases in the following order: H₃PW₁₂O₄₀ > H₄SiW₁₂O₄₀ > H₃PMo₁₂O₄₀ > H₄SiMo₁₂O₄₀ [26]. All these HPA combinations are soluble in alcohol and are difficult to be separated from water or alcohol, especially under microwave irradiation. To overcome this problem, Zhang et al. [27] added the other ionic salts of alkaline cations such as Cs⁺, NH₄⁺, Ag⁺ and Na⁺ to the system containing H₃PW₁₂O₄₀. Thus H⁺ was substituted with the alkaline cations. The alkaline cations provided excellent efficiency under the microwave because they are not soluble in organic solvents and water. They exhibited similar activities compared to the parent acid in acid-catalyzed reactions. This new heterogeneous catalyst, can provide micro and mesopores with a high surface area and a change in the number of available surface acid sites. In addition, larger monovalent ions gave better results (96.7% at only 10 s under microwave irradiation) [27].

Ionic catalysts have also received attentions since they are able to catalyze various polyesterification reactions under microwave irradiation. Among them, diphenylammonium salt catalysts have a prominent ability in catalyzing transesterification of vegetable oils into biodiesel. Furthermore these types of catalyst are recyclable and thermally stable [28]. Majewski et al. [25], used three different types of DPA called DPABS, DPAMs, and DPATs for the first time. They identified these types, as suitable acid catalysts; which can be jointed with microwave technology to produce a more expedient and less wasteful product. The results are reported in Table 3 to clarify the related situation. Lin et al. [28] also have studied the use of 4-allyl-4-methylmorpholin-4-ium bromine (IL; [MorMeA][Br]) as an ionic liquid catalyst under the microwave heating to improve biodiesel yields from waste cooking oil. They have found that ionic catalyst can increase the reaction time by 9% and decrease the use of NaOH catalyst by 0.25 wt%. In another work, Lin et al. [29] have also used the (IL; [MorMeA][Br]) as a catalyst. They have reported that the reaction yield increased with increasing [MorMeA][Br] catalyst amount (from 0.00 wt% to 1.00 wt%) and then decreased with greater increasing catalyst amount (1.00–1.50 wt%). They reached to the maximum yield of (99.4%) with IL1 NaOH0.75 catalyst (1 wt% [MorMeA][Br] 0.75 wt% sodium hydroxide (NaOH)), was achieved at a methanol-to-oil molar ratio of 9, a reaction time of 6 min and a microwave temperature of 70 °C.

Unfortunately, there is not enough information in transesterification using these catalysts. The results indicate that an excessive amount of catalyst may increase the biodiesel yield; however, it raises the formation of glycerin caused by saponification. In addition, a high catalyst concentration may result in increase in the interaction of the other compounds and also higher production of byproducts which leads to reduction in the biodiesel yield. Thus it may hinder the catalyst and increase component removal costs from the reaction medium at the end of the process. Furthermore, excess catalyst may raise bulk viscosity and result in the formation of gels, which is an obstacle on glycerin separation. By the dilution of ethyl esters, the reaction yield diminishes [11]. The other problem is the corrosive nature of the catalysts. For this reason,

Table 4
Heterogeneous alkaline catalysts used for transesterification reaction assisted by microwave irradiation.

Power/W	Feedstock	Alcohol/oil molar ratio	Temperature (°C)	Catalyst/loading (wt%)	Time (min)	Yield (%)	Remarks	Ref
800 W	Dry algal	Methanol(12:1)	60–64	KOH 2% (wt/vol)	4–5	80.13%	Optimum 254.4 energy consumption	[7]
SCM	Wet algal	Methanol(9:1)	255 1200 psi	Without	25	84.15%	Optimum 600 kJ energy consumption	[7]
1000	Yellow horn oil	Methanol(8:1)	60-high alkaline	Amberlite IRA-900-5%(resin)	90	96.5%	Maximum	[8]
1000	Yellow horn oil	Methanol(8:1)	60-weak alkaline	Amberlite IRC-93-5%(resin)	90	57.4%	Maximum	
1000	Yellow horn oil	Methanol(8:1)	60-high alkaline	Amberlite IRA-900-5%(resin)	75	95.24%	Optimum	
CON	Yellow horn oil	Methanol(8:1)	60- high alkaline	Amberlite IRA-900-5% (resin)	180	25.8%	Maximum	[8]
900 W	Palm olein oil	Methanol(18:1)	60	CaO (powder)	4	96.7%	Maximum & optimum	[38]
300 W	Soybean oil	Methanol(7:1)	65	CaO (nano) (3%)	60	96.6%	Optimum	[39]
	Soybean oil	Methanol (7:1)	65	CaO (nano) (3%)	15	56.2%	Maximum	
	Soybean oil	Methanol(7:1)	65	CaO (nano) (3%)	30	82.8%	Maximum	
CON	Soybean oil	Methanol(7:1)	65	CaO (nano) (3%)	15	22.1%	Maximum	[39]
	Soybean oil	Methanol(7:1)	65	CaO (nano) (3%)	30	35.4%	Maximum	
40W	Castor bean oil	Methanol(6:1)	60	Al ₂ O ₃ /50% KOH	5	95%	Maximum	[72]
CONV	Castor bean oil	Methanol(6:1)	60	Al ₂ O ₃ /50% KOH	60	95.5%	Maximum	[72]
1000 W	Rape seed oil	Methanol(9:1)	103	Ba(OH) ₂ H ₂ O(1.5%)	10	99%	Maximum	[37]
	Rape seed oil	Methanol(9:1)	60–65	Ba(OH) ₂ H ₂ O(0.5%)	17	97%	Maximum	
	Rape seed oil	Methanol(9:1)	60	Ba(OH) ₂ H ₂ O(1.5%)	15	98%	Maximum	
CONV	Rape seed oil	Methanol(18:1)	60	No Catalyst	60	81%	Maximum	[37]
900W, 21 sec on, 9 s off	Microalgae lipids	Methanol(2:1 v/ v)	60	SrO (0.3)	7	99.9%	Optimum Conversion 37.1% yield	[50]
Sonication	Dry biomass						5 min for heating	
	Microalgae lipids	Methanol(2:1 v/ v)	50	SrO(0.3)	7	90%	2 min for reaction Optimum	[50]
20 kHz						Conversion 30.9% yield	5 min for heating 2 min for reaction	
1100 W	Soybean oil	Methanol(6:1)	60	SrO-0.276 g KOH-0.15	40 s	SrO–97% KOH–81%	Maximum	[34]
1100 W	Cooked oil	Methanol(6:1)	60	SrO-0.276 g KOH-0.15	40 s	SrO–99% KOH–83%	Maximum	[34]
600 W	soybean oil	Methanol(2:1)	65	(10 wt%)	30 min	95%	Maximum	[36]
400 W	Rapeseed oil	Methanol(11:1)	34.5 °C,	Calcined sodium silicate (4%)	5 min	95.8%	Maximum	[73]
	Jatropha oil		500 bar			92.8%	Maximum	
20 W	Soybean oil	Methanol(10:1)	-	Amorphous silica oxide with 10 wt% of sulfonic groups	3 h	96%	Maximum	[74]

A small amount of Sr(OH)₂ exists within the commercial SrO which leads to dissolution of the hydroxide group. Therefore it is not considered as a 100% heterogeneous catalyst [50].

an optimum concentration under microwave irradiation should be used, which depends on the catalyst type and practical operations. Most of the researches illustrated that there is no report on positive effect of the reaction conversion for catalyst concentration above 2% (refer to Tables 2 and 3). They found that the conversion decreases by higher catalyst concentrations, which may be due to the production of water consequently followed by soap formation. Some of them even introduced the amount of 1.5% as the maximum allowable catalyst concentration [30–32].

3.2.2. Effects of heterogamous catalysts

In the field of heterogeneous catalysts, the internal and external sites of the solid catalyst are the places where reaction occurs. Thus the activity of the heterogeneous catalysts under the microwave spectrum is extremely influenced by the microwave absorbing ability and may result in hot spots production. The temperature in these hot spots is much higher than that in the reaction mixture bulk (above 1200 °C) [14], which increases the reaction and conversion rate. Thus, the mass transfer resistance is

counteracted by high reaction temperature caused by microwave in the case of heterogeneous catalyst [20].

As indicated by many authors and as shown in Tables 4 and 5, in heterogeneous type, the catalyst should be from polar material such as sulfuric acid. At the same time, the catalyst carrier should be from a material with a strong microwave absorbing property such as activated carbon, which is one of the best absorbing materials with steady physical properties and significant surface area. Furthermore, it has a high rate of temperature rise [14] that could be heated under microwave radiation [20,33]. Yuan et al. [20] used a heterogonous catalyst based on the above conversation (H₂SO₄ on carbon active). They explained that since microwave radiation has an instantaneous and selective heating function, the generated hot spots can absorb catalyst and then they reached for yield of 94%. Wang et al. also used K₂SiO₃ as a nonconventional basic solid on carbon active since this material can effectively distribute on the surface of the support. By this combination, they could reach to the conversion rate of 96.7% at the equilibrium point; however, the reaction did not reach equilibrium by conventional heating even after 2.5 h [33].

Table 5
Heterogeneous acidic catalysts used for transesterification reaction assisted by microwave irradiation.

Power (W)	Feedstock	Alcohol/oil molar ratio	Temp. (°C)	Catalyst, loading/wt%	Time/min	Yield (%)	Remarks	Ref
1000	Yellow horn oil	Methanol(8:1)	60- high acidic	Amberlyst-15 5% (resin)	90	83.5	Maximum	[8]
1000	Yellow horn oil	Methanol(8:1)	60- weak acidic	Amberlite IRC-72-5% (resin)	90	55.7	Maximum	
CON	Yellow horn oil	Methanol(8:1)	60- high acidic	Amberlyst-15 5%(resin)	180	23.6	Heated by oil bath	[8]
CON	Yellow horn oil	Methanol(8:1)	60- high acidic	Amberlite IRC-72-5% (resin)	180	25.8		
150	Soybean oil	Methanol(30:1)	65	(K ₂ SiO ₃ /C) 24 wt%	30	57.77	Maximum	[33]
	Soybean oil	Methanol(30:1)	65	(K ₂ SiO ₃ /C) 24 wt%	60	84.53	Maximum	
	Soybean oil	Methanol(30:1)	65	(K ₂ SiO ₃ /C) 24 wt%	90	96.50	Maximum	
	Soybean oil	Methanol(30:1)	65	(K ₂ SiO ₃ /C) 24 wt%	120	95.66	Maximum	
CON	Soybean oil	Methanol(30:1)	65	(K ₂ SiO ₃ /C) 24 wt%	60	38.55	Maximum	[33]
	Soybean oil	Methanol(30:1)	65	(K ₂ SiO ₃ /C) 24 wt%	90	77.91	Maximum	
	Soybean oil	Methanol(30:1)	65	(K ₂ SiO ₃ /C) 24 wt%	120	93.77	Maximum	
	Soybean oil	Methanol(30:1)	65	(K ₂ SiO ₃ /C) 24 wt%	150	96.98	Maximum	
	Soybean oil	Methanol(30:1)	65	(K ₂ SiO ₃ /C) 24 wt%	180	96.78	Maximum	
100–200	Oleic acid	Methanol(20:1)	60	Amberlyst 15 dry 10 wt %	15	39.9		[43]
	Oleic acid	Methanol(20:1)	60	Amberlyst 15 dry 10 wt %	15	66.1	Continuous pulse ^a period of 2.5 ms (or 400 Hz repetition rate)	
500	Yellow horn oil	Methanol(12:1)	60	Heteropoly acid (HPA)	10	96.22	Optimum	[27]
	Yellow horn oil	Methanol(20:1)	60	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ 1%	10	96.16	Maximum	
500	Yellow horn oil	Methanol(12:1)	60	Heteropoly acid (HPA)	60	97.3	Optimum	[27]
	Yellow horn oil	Methanol(20:1)	60	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ 1%			Maximum	
200	Castor oil	Methanol(12:1)	65	H ₂ SO ₄ /C 55% (loading)-5% (catalyst)	10 20 30 60 90	36.0269 52.862 82.1549 94.2761 92.2559	Optimum Maximum Maximum Maximum Maximum	[20]
CON	Castor oil	Methanol(12:1)	65	H ₂ SO ₄ /C 55% (loading)-5% (catalyst)	10 20 30 60 90	20.202 23.9057 31.9865 46.1279 50.1684	Optimum Maximum Maximum Maximum Maximum	[20]
500	Yellow horn oil	Methanol(15:1)	60	(NH ₄) ₃ PW ₁₂ O ₄₀ 1%	10	95.3	Maximum	[27]
				Ag ₃ PW ₁₂ O ₄₀ 1%	10	95.7	Maximum	
				Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ (HPA) 1%	10	96.7	Maximum	
				Na ₃ PW ₁₂ O ₄₀ 1%	10	93.2	Maximum	
40	Castor bean oil	Methanol(6:1)	60	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ 1% SiO ₂ /50% H ₂ SO ₄	10 30	96.22 95	Optimum Maximum	[72]
220	Castor bean oil	Ethanol(6:1)		SiO ₂ /50% H ₂ SO ₄	20	> 95	Maximum	
220	Castor bean oil	Ethanol(6:1)		SiO ₂ /50% H ₂ SO ₄	25	95	Maximum	
CON	Castor bean oil	Methanol(6:1)	60	SiO ₂ /50% H ₂ SO ₄	48 h	78	Maximum	[72]
	Castor bean oil	Methanol(6:1)		SiO ₂ /50% H ₂ SO ₄	3 h	95.5	Maximum	
	Castor bean oil	Ethanol(6:1)		SiO ₂ /50% H ₂ SO ₄	6 h	95	Maximum	

Yellow horn oil (*Xanthoceras sorbifolia* Bunge); SCM—supercritical methanol.

^a Under pressure of 3.5 bar.

Supported alkaline earth metal oxides are the other groups of catalysts which can be applied with microwave effectively. Their activity in these groups is with the following range BaO > SrO > CaO > MgO. Among them, BaO is not suitable for transesterification reaction since it is noxious and can be dissolved by methanol. CaO and MgO provide a satisfying reaction rate due to their strong basic sites; however, they suffer from their low activity in the production of biodiesel from vegetable oils. But, many researchers have reported CaO as a solid strong base catalyst under the

microwave irradiation. SrO can catalyze transesterification reactions easily. It could decrease the reaction time to about 40 s with the highest conversion yield of 97%, while in a similar situation, KOH could reach only 81% yield of bio-diesel production [34]. However, the most important weakness of this group is the sensitivity to methanol. Because the active ingredients are corroded by methanol and they represent short lifetimes [35]. Thus, CaO is the most popular catalyst among them due to its longest lifetime, cheapest price and mildest reaction condition.

Ion exchange resins are the most important groups of heterogeneous catalysts. In order to test the heterogeneous catalytic actions, Li et al. [8] investigated four different ion exchange resins including Amberlyst-15, Amberlite IRA-900, Amberlite IRC-72, Amberlite IRC-93 and compared them with homogenous alkali catalyst (KOH). They could increase the reaction yield of heterogeneous catalyst to 96.3%, which was similar to the homogenous by microwave system. But without microwave system, the conversion yield of this heterogeneous catalyst diminished to 23.6% even in the longer time of 180 min. Naturally, swelling properties of the ion exchange resins control the catalytic activity and reactants accessibility to the active sites. Microwave irradiation in comparison with the other methods of transesterification, can accelerate the movements of molecules by the electromagnetic field. Therefore, there is a high tendency to employ alcohol which result in a remarkable swelling phenomenon [8].

Recently, Li et al. [36] developed a solid base catalyst by the sodium potassium tartrate doped zirconia to biodiesel synthesis and tested it under the microwave irradiation. They have found that the catalyst of $2.0(n_{\text{Na}}/n_{\text{Zr}})$ and calcined at 600 °C showed maximum yield of 94.75%. However they could achieve the maximum yield of 42.33% under the conventional heating.

In order to compare the performance of heterogeneous catalysts with those used in homogeneous phase, Yuan et al. [20] used both heterogeneous catalyst $\text{H}_2\text{SO}_4/\text{C}$ and homogeneous catalyst H_2SO_4 . They used 5 wt% mass ratio of catalyst to castor oil, 55 wt% H_2SO_4 loading amounts of catalyst and molar ratio of 12:1 for methanol to castor oil, at 338 K [20]. They obtained equivalent yield of FAME after 60 min with the maximum rate of 94%. Mazzocchi and Modica [37] compared heterogeneous $\text{Ba}(\text{OH})_2\cdot\text{H}_2\text{O}$ catalyst with homogenous NaOH catalyst. They observed similar results in presence of either sodium or barium hydroxides when microwave heating was employed (both 99%). However the difference of FAME yields was observed under conventional heating and homogenous based catalyst provided better results (99.4% vs. 98.1%).

Regarding to Tables 4 and 5, the last important issue is the value of optimum loading in heterogeneous systems, which is higher than homogenous ones. Khemthong et al. [38] reported catalyst loading of 15 wt% which result in suitable reaction conversion rate. Less than this percentage, especially below 5 wt%, is not sufficient to catalyze the transesterification and cannot produce the biodiesel yield higher than 10%. However, this value decreases until 3% in the Nano scale [39].

3.2.3. Enzymic catalyst

Enzymes are the final group of the catalysts, which are also able to catalyze the transesterification process for biodiesel production. But the application of these types of catalysts is so limited due to their sensitivity to high temperature. Due to this limitation, these catalysts should be used in a narrow and very low temperature. Thus there is not enough publication in this field. Only Nogueira et al. [40] investigated the synthesis of macauba (*Acrocomia aculeata*) oil and ethanol using Lipozyme IM and Novozyme 435, in order to evaluate the effect of microwave presence in catalytic activity in the group of enzymic catalyst. In spite of the fact that they applied the low range temperatures of 30–40 °C, they found deactivation effects due to microwave by investigating the interaction between the temperature and reaction time.

3.2.4. Non-catalytic transesterification

The microwave-assisted transesterification reaction of algal biomass to yield alkyl esters gets a great attention recently. The microwave supports this type of operation by evaporation of alcohol due to the strong microwave interaction of the material

and enhancement of reaction by a thermal effect. In a new research, Patil et al. [41] has proposed an integrated approach to convert a lipid-rich dry algae into fatty acid ethyl esters under microwave-mediated supercritical ethanol conditions with a non-catalytic transesterification approach. They could extract of the algal biomass and convert it into algal biodiesel in a relatively short reaction time using microwave irradiation. Finally they could obtain to highest yield of 33% under the situation of 265 °C, ca. 80 bar, at algae to ethanol (wt/vol) ratio of 1:12 within 20 min of reaction time under controlled power between 1400 and 800 W [41]. In another work, Patil et al. [42] repeated their previous work using a lipid-rich wet algae increase to the maximum value of 30.9% at algae to ethanol (wt/vol) ratio of 1:9 and the pressure of 65 bar and the temperature of 245 °C. In another study, Patil et al. [7] have compared the direct conversion of algal biomass into biodiesel using microwave-assisted (MW) transesterification and supercritical methanol (SCM) methods. They have reported that the microwave-assisted approach reduced the extractions time of algae with a higher efficiency. Furthermore, it improves the transesterification reaction yield. While the non-catalytic supercritical methanol method produces highly purified extracts, and reduces energy consumption of separation and purification steps.

4. Effect of operational condition

As it is clear, temperature, reaction time and alcohol to oil molar ratio, microwave irradiation power as well as catalyst concentration are the most important parameters for biodiesel production. There were more than 1000 available similar data in the literature, and most of them focused on the investigation of the mentioned parameters. This study tried to gather the highest and most optimal results in Tables 2–5. But since the statistical investigation of whole data is not possible easily, an empirical model is correlated to describe the reaction yield of transesterification for biodiesel production. The model is based on fitting a wide range of different experimental results that has used the 1% solution of alkaline catalyst. As mentioned in Section 3.2, the majority of published works focused on alkaline catalyst due to the corrosive nature of the acidic one and its higher reaction time. The model analyses the importance of key process variables such as temperature, alcohol to oil molar ratio and reaction time under the microwave irradiation. In addition, this model is applicable for the prediction of conversion yield with the operational parameters of the temperature between 40 and 80 °C, time between 3 and

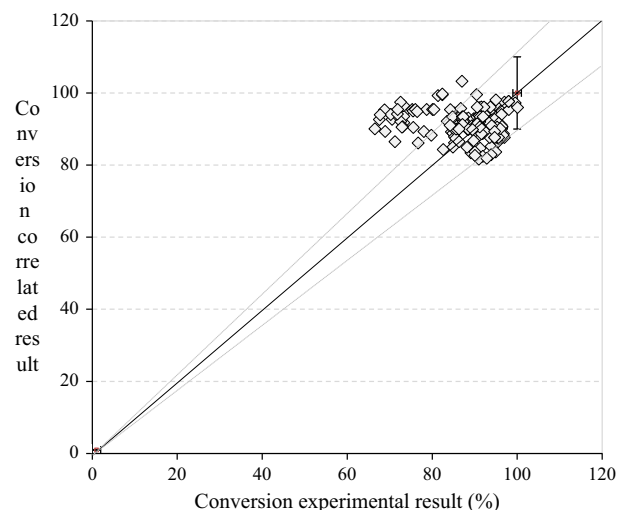


Fig. 4. The predicted result of conversion versus experimental data.

15 min and alcohol to oil molar ratio between 3 and 12.

$$Yield = 72 \times T^{0.073} \times R_m^{0.0107} \times t^{-0.05268} \quad (2)$$

It was found that the order of significant factors for biodiesel production is in the following range: reaction temperature > reaction time > alcohol to oil molar ratio. However, in biodiesel production under the microwave irradiation, increase in the reaction time higher than 5 min may lead to a negative effect on reaction yield. Since the time limitation of the model is between 3 and 15 min, this negative effect is clearly observed by the negative power of the time parameter. A decline in the reaction conversion by increasing the reaction time has been reported by most of the authors. The predictive power of the developed model was checked for a wide range of parameters value and operational conditions, a very good satisfaction between model simulations and experimental data is observed with deviation of $\pm 8\%$ (Fig. 4)

4.1. Effects of microwave power and energy consumption

Another challenging point in the field is energy consumption, which is an economic parameter. In conventional heating of transesterification process, heat transfer occurs via radiation and conduction from the source of heating and via convection and conduction within the material. Thus, the conventional heating takes longer time for preheating and reaction and also it consumes a higher energy, which depends on the thermal conductivities of the materials [15,19]. In the microwave-assisted process, energy can penetrate within materials. Then a molecular friction is generated, caused by the conductive migration of dissolved ions and the dipolar rotation of polar solvents and intensifies the localized heating. In addition, by a rapid transfer of energy through molecular interaction with the electromagnetic field, a volumetric distribution of heat energy is produced which has a significant effect on the yield of transesterification [9]. Thus the higher irradiation power enhanced the reaction yield. If it goes too high, it can offer superfluous energy to the solvent and raw materials and may damage the organic molecules such as triglycerides, which are cleaved to FFA. Even it may make molecular interaction too disordered and drastic [9,11]. As an example, under the microwave spectrum, the triglyceride structure becomes flat and dipolar moment decreases as explained before (refer to Fig. 2). In order to investigate the effect of MW power, Zu et al. [9] used different powers of microwave irradiation in the range of 100, 300, 500, 700 and 1000 W. The reaction was controlled within 6 min at the temperature of 60 °C, 1 wt% solution of KOH as the catalyst and methanol/oil molar ratio of 6:1. They reported that increasing the irradiation power till 500 W causes the growth of reaction conversion. But higher than that especially after 700 W, results in declining of conversion yield. This point is related to the raw materials, which have different appropriate irradiation power. In other words, destroyed molecules can decrease the reaction conversion.

Patil et al. [23] expressed that the energy consumption in microwave irradiation method is generally 23 times lower than that in the conventional method. As an example, for many reasons energy requirements for supercritical methanol process are much higher than for the microwave assisted method. Supercritical methanol process operates at high temperature and pressure and with reaction times significantly longer than the microwave assisted method [7]. For a lower energy consumption in the microwave assisted process, transferring the microwave power to various reactants is not enough and the method of applying is also important. Recently, pulsed microwave is used as a new suggestion. Kim et al. [43], used a square-pulsed microwave with a 400 Hz repetition with the 10–20% duty cycle with the same energy compared with continuous. Using this method they could

save energy and enhance the reaction rate from 39.9% to 66.1% during esterification at an exact similar situation of continuous power. Thus pulsed microwaves with repetitive strong power can be more efficient than continuous microwave with mild power [43]. However there is not enough published work using this technique especially in transesterification; in introduced correlated model, only the continuous irradiation is considered.

Since microwave irradiation power affects temperature and reaction time consequently, in the introduced correlated model, the direct influence of irradiation power is ignored and it is considered by the effect of two mentioned key parameters due to prevention of employing microwave power twice.

4.2. Effects of alcohol to oil molar ratio

According to the chemical dynamics, each mole of methanol and one-third mole of a triglyceride made 1 mole of biodiesel in the transesterification reaction. But in practice, the transesterification reaction is reversible, thus increasing of alcohol may lead to accelerate the reaction by shifting the reversible reaction forward. Furthermore, alcohol (especially methanol) is a strong medium for absorbing microwaves, so a higher amount of alcohol may absorb greater microwave energy and decrease the microwave consumption energy [11], and it can influence the final temperature of the media which is so effective on reaction conversion. In addition, excess alcohol results in a better solubility of biodiesel and glycerol [11]. Encinar et al. [13] reported that the final temperature of reaction is also more affected by alcohol/oil molar ratio at the high power of microwave (> 200 W). He also explained that by using

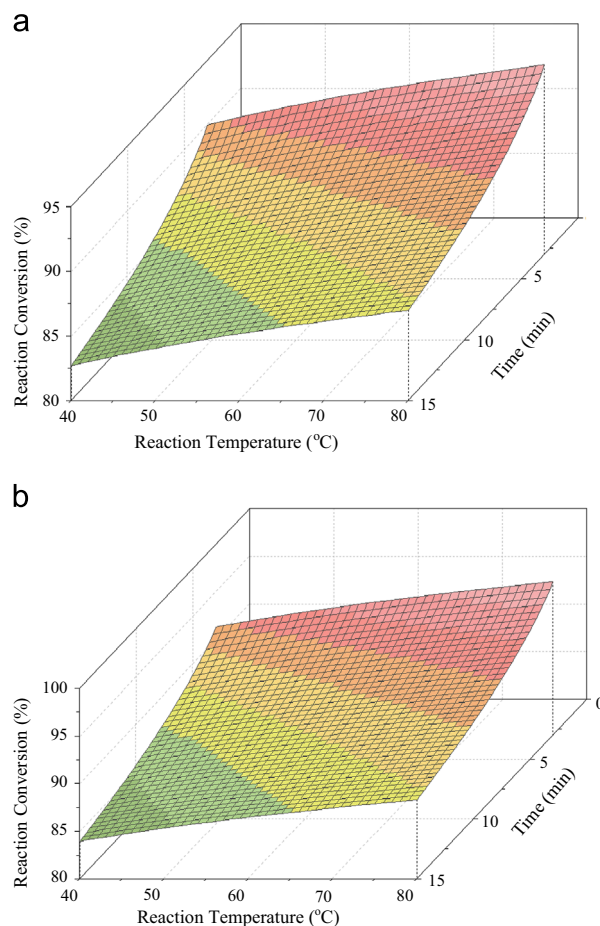


Fig. 5. Reaction conversion versus time and temperature at: (a) alcohol to oil molar ratio of 3 and (b) alcohol to oil molar ratio of 12.

the alcohol to oil molar ratio of stoichiometry (3:1), no more than 75% of conversion yield is achieved. Therefore, in order to reach a greater ester production than equilibrium point, an extra amount of alcohol was needed [13]. Besides, when the amount of alcohol increases, higher energy is required for alcohol vaporization; so for the same time of microwave radiation exposure, the temperature enhancement is lower. It means by increasing this ratio, the gradient of temperature decreases [13]. However, higher amount of alcohol may lead to three problems; firstly, excess loss of the solvent or worsen rates of solvent recovery. Secondly, high basic alcohol concentrations may also diminish the existence of the catalyst in the media [7]. Finally, it produces several mass transference obstacles during the transesterification process at low temperature since alcohol is not soluble in triglycerides at molar ratios over 3:1. Generally, the speed of the reaction at the beginning time is controlled by the diffusion of reagents between the phases. Increasing the alcohol/oil molar ratio decreases the contact between the phases consequently followed by diffusion problems. These problems are diminished at higher temperature when alcohol is evaporated and the contact between the phases increases [13].

Then some authors suggested an optimum molar ratio of alcohol to oil between 1:6 and 1:9 which has a positive effect on the yield and higher than these levels has a negative effect under

MW irradiation. Some authors even suggested related value up to 1:12, as mentioned in Tables 2–5. If the ratio is lower than 5, there is not enough interaction between methanol/oil [30]. The high molar ratio increases the rate of the reversible reaction forward by accelerating the contact area between alcohol and lipid, which leads to higher yield of FAME [13,30].

This optimum value is also observed in the other transesterification methods such as supercritical method [7,11]. It is worth noting that this optimum value in microwave system is lower than conventional heating while the ratio between 1:9 and 1:30 is more commonly applicable [44]. This optimum value in the reaction vessel containing heterogeneous catalyst, depends on the catalyst free sites, increases in the range of 15:1–18:1 [38]. To study the effects of temperature and time on biodiesel yield in our model's graph, the molar ratio of alcohol to oil was fixed as 3:1 and 12:1. By considering Fig. 5, we see that at the reaction time of 3 min and the temperature of 80 °C, increasing the alcohol to oil molar ratio raises the reaction conversion from 94.5 to 96.5, while at the reaction time of 15 min it changes from 87% to 88%. Another worth mentioning point in the last figure is the role of alcohol to oil molar ratio, which is not depended on temperature.

4.3. Effects of reaction time

Since the transesterification is a three-step reaction, selection of a proper transesterification time is required to guarantee the completion of the reaction [9]. In general, suitable reaction times provide adequate interaction of the microwave effect with the reaction mixture. It follows by a higher reaction temperature and results in better yields of extraction and reaction, but lower reaction times decrease the contact of reactant mixture exposed to the microwave radiation [23]. Overall, decreasing the reaction time is the main advantage of using microwave. However, extension of reaction times enhances the exposure of microwaves to the reaction media. Theoretically, Arrhenius equation ($K=A e^{-\Delta G/RT}$) describes the reaction rate by two factors: ΔG , which is Gibbs free energy of activation and A , which is the pre-exponential factor. The latter is the molecular mobility, which increases the reaction rate through the frequency of the vibrations of the molecules at the reaction interface. It also can be changed by affecting the free energy of activation [7]. Thus in microwave assisted systems, by increasing the A factor, reaction rate increase may lead to decreasing the reaction time. Refer to Tables 2–5, it seems that microwave irradiation can speed up the reaction and reduce the reaction time to 4–5 min with the microwave power of 1200 W for the complete extraction and transesterification reaction. Having a reaction time higher than 5 min may result in greater losses of solvent and energy and larger formation of by-product. But this situation may be changed by microwave power. Similarly, Azcan and Danisman [45] found that the yields of rapeseed oil biodiesel were 92.2%, 92.7%, and 92.0% for the reaction times of 1, 3 and 5 min, respectively, with 1.0 wt% NaOH, methanol-to-oil molar ratio of 6 and a microwave power of 1200 W [11]. By decreasing the power until 200 W, the suitable time increased up to 15 min [13]. However, this point has been less reported in case of esterification of high FFAs oil under microwave condition [16].

Kim et al. [46] concluded that for a conversion rate higher than 90% by microwave heating, reaction time lessens nearly to 1/7 of the conventional heating. In order to further reduce the time to reach a fixed temperature, Manco [14] used different pebbles: ceramic pieces, glass beads and carborundum. They could decrease the reaction time: from 540 s without pebbles to 90 s with carborundum in microwave system. They confirmed their observation by using the pebbles in the reaction mixture. It caused the production of regular heating, prevention of overheating and the reduction of the required reaction time. The study in the process of

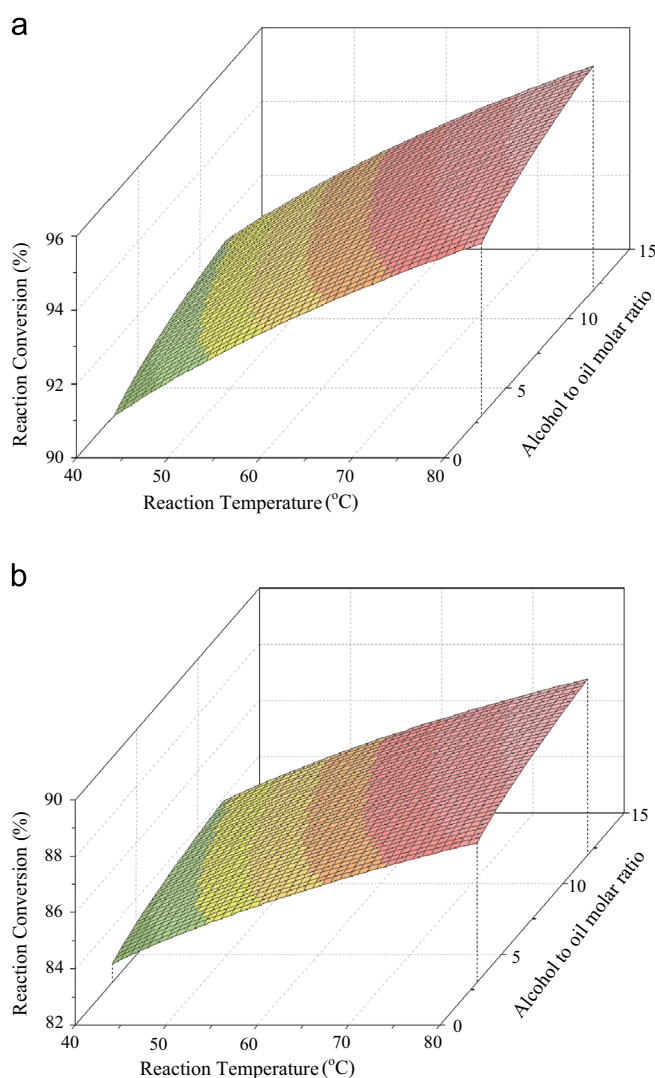


Fig. 6. Reaction conversion versus alcohol to oil molar ratio and temperature at: (a) time of 3 min and (b) time of 15 min.

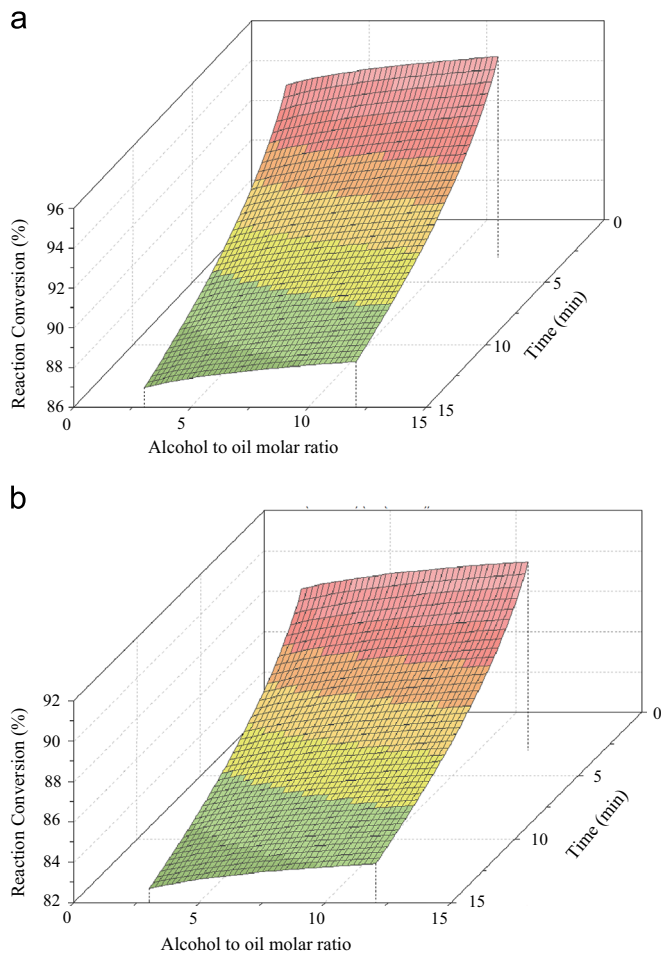


Fig. 7. Reaction conversion versus alcohol to oil molar ratio and time at: (a) at temperature 80 °C and (b) at temperature 40 °C.

transesterification by Hsiao [7], pointed out that the use of CaO nanopowder, ensures greater efficiency with the lower reaction time than that of CaO powder under the microwaves [39]. However, these exceptions were not considered in our model.

In another work Cheng et al. [47] applied microwave irradiation in order to decrease the time of lipid extraction and transesterification reaction. They have reported that the kinetic rate of converting wet microalgae into biodiesel via the two-step method using conventional heating is approximately six times slower than that via the one-step method using microwave irradiation.

Controller systems are the other important factors in decreasing the reaction time during the transesterification process. Traditional controllers cannot reach to a good efficiency when the process to be controlled is characterized by parameter uncertainties and high nonlinearities. Therefore it requires the effective controllers to handle multivariable problems and to adapt the time varying dynamics.

Recently Wali et al. [48] applied on line intelligent controllers (Neuro-Fuzzy, Fuzzy Logic and Adaptive) to control the real time and temperature control in advanced biodiesel microwave reactor. They have indicated that Fuzzy control is able to regulate in minimal overshoot but the ANFIS controller is more efficient to parameter variations when compared to the Fuzzy controller.

The two-second correlation graphs (Fig. 6a and b) show the parallel importance of alcohol to oil molar ratio and reaction temperature at the fixed time of 3 and 15 min, respectively. As observed, the effect of alcohol to oil molar ratio and temperature in the reaction time of 3 min is more prominent than in 15 min,

because the graph is sharper. As mentioned in the previous paragraph, this is due to the negative effect of time, which is much higher than the alcohol to oil molar ratio. Also at the time of 3 min, the reaction yield is between 90% and 96% while in the similar situation but at the time of 15 min, the reaction yield is between 82% and 90%. Then increasing the time has the negative effect on reaction yield and causes reduction in the conversion yield. If it supposed that the optimum reaction time is within 3–5 min, increasing about 10 min (until the reaction time of 15 min) will lead to decreasing about 5% of reaction yield. This affect is more prominent at higher alcohol molar ratio. In addition, it obtained opposite results in the temperature rate up to 80 °C, which leads to increasing the yield of biodiesel production.

4.4. Effects of temperature

It is observed that the reaction conversion is more dependent on the final temperature than the residence or reaction time. However, the temperature significantly is influenced by microwave power, components absorption ability and residence time; therefore, all variables must be considered [13]. In microwave systems, reaction temperature rises very fast from 30 °C to 78.5 ± 1.0 °C in the first 30 s of the reaction and then slowly increases to 84 °C within 60 s. So the effective temperature in the reactor is started from 78.5 °C. Generally, in transesterification reaction, a higher reaction temperature helps to decrease the time and increase the reaction yield.

Muley and Boldor [22] have found that the decreasing rate of dielectric constant declines as the temperature rises which is related to the kinetic energy of molecules. Therefore the response to the changing electric field is faster, which increases the realignment process, enhancing the dipolar rotation of molecules and the dielectric constant of the material compared to lower temperature. Terigar et al. [49] have also reported that at higher temperature, dipolar rotation is more prominent causing a shift in the location of where dielectric constant decreases.

In microwave-assisted process, as mentioned before, the reaction is occurring in a real temperature, which is much higher than bulk temperature; but the bulk temperature is still important especially as a controller item. In a very high bulk temperature, reduction of methyl ester content is reported [13]. It is due to cracking followed by oxidation of the methyl esters to ketones, aldehydes and lower-chained organic fractions. Zu et al. also concluded that at high temperature level before completion of the transesterification, the saponification of glycerides by the alkaline catalyst tends to accelerate which has a negative effect on process yield [9].

In the last Fig. 7a and b, the interaction between the time and alcohol to oil molar ratio is investigated at the temperature of 80 °C and 40 °C. The maximum yield is observed at the reaction time of 3 min, the temperature of 80 °C and the molar ratio of 12. The least conversion yield is obtained at the temperature of 40 °C with the stoichiometric alcohol molar ratio within 15 min. Generally, at the reaction time of 3 min, increasing the temperature from 40 to 80 °C, may raise the reaction yield by 6%. This increase is about 5% at 15 min of reaction time. From comparing the two graphs, the average of the reaction conversion under the microwave at the temperature of 80 °C is nearly 5% higher than at the temperature of 40 °C. But this result is as an average; because at the reaction time of 3 min, which the highest conversion is achievable, this difference increases to higher than 7%.

Finally, the investigation of Tables 2–5 show that most authors reported that the temperature range of 65 °C to about 90 °C, has the most and best effect on biodiesel production (from 88 to 98w/w). Although this temperature is higher than alcohol boiling point, it is observed that common solvents boil at higher

temperatures in the presence of microwaves; the difference measured is up to 5 °C for water, 19 °C for methanol and about 36 °C for tetrahydrofuran and acetonitrile [15]. In these conditions, alcohol can be evaporated which provides a great contact with oil in the shorter reaction time. However, this thermal gradient has the positive effect up to the alcohol boiling point and at final higher temperature, the reaction rate decreases slightly caused by decreasing the contact between alcohol and oil [13]. This problem is because of the change in the volume fraction ratio between alcohol and oil, which is corrigible via controlling the volume fraction by additional injection.

5. Conclusion

As summarized, polar molecules under the microwave spectrum try to align themselves with the magnetic field lines, which are changed continuously. Thus the charged ion or molecular dipoles which interact with the changing magnetic field have to rotate rapidly. It results in the generation of energy in the form of heat due to molecular friction under MW irradiation. Transesterification process assisted by microwave technology is followed by a higher reaction temperature cites called hot spots. The review indicated that reaction in this situation is taken place in a temperature much higher than bulk temperature. Therefore, more efficient heating can be obtained compared to the usual conventional heating even more than sonochemical or supercritical reaction. This energy acts on the molecular scale [50]. Under this situation, a reduction in reaction time from about 70 min (in conventional heating) to about 3 min (in MW heating) with a better production yield is obtained. Furthermore, the review indicated that methanol is the best choice among the other alcohols since it is the most polar and shortest chain alcohol. Therefore, it can easily absorb MW energy increases the temperature, reaction rates and yields and decreases catalyst requirement to less than ten-fold [19]. A less requirement to alcohol in transesterification under MW in contrast with conventional heating is another point. Therefore, the mixture of methanol, and NaOH or KOH is suggested as the best mixture; since it contains both polar and ionic components, can bring about a rapid heating under microwave irradiation and efficient reaction yield. In addition, an empirical model is generated to investigate, summarize and predict the effect of operating parameters. The model is based on fitting a wide range of different experimental results for homogeneous alkaline catalysis. The model briefly shows the reaction time between 1 and 3 min, at the reaction temperature of 65–90 °C and alcohol to oil molar ratio of 6 to 9 (using homogenous catalyst) under the irradiation power of 1200 W are the optimum situation. The model provides satisfied results even by using the other homogenous catalysts with maximum error of $\pm 8\%$.

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